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Comparison of Electron Beam and Pulsed Corona Processing of Carbon Tetrachloride in Dry Air Streams

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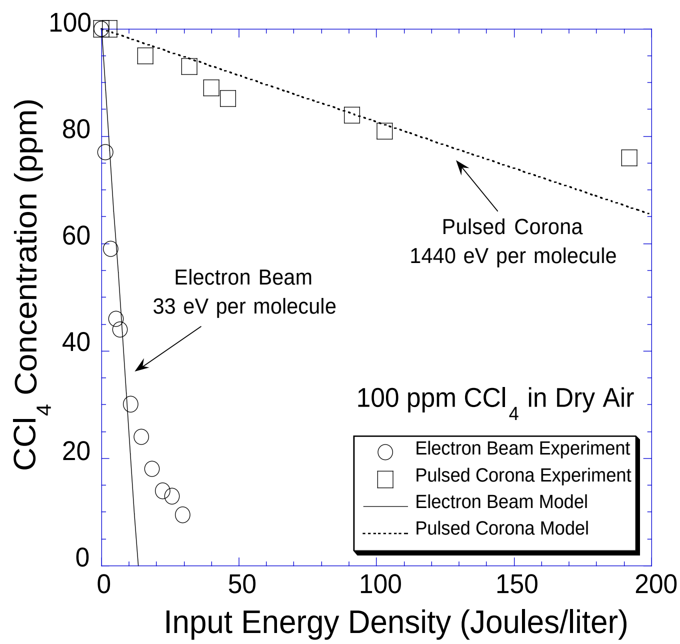
This paper presents a comparison of the specific energy consumption for electron beam and pulsed corona processing of dilute concentrations of carbon tetrachloride (CCl_4) in atmospheric-pressure air streams. In non-thermal plasma processing of this gas mixture, the rate limiting step in the decomposition of CCl_4 is determined by the dissociative attachment of CCl_4 to the thermalized electrons in the created plasma: $e + CCl_4 \Rightarrow Cl^- + CCl_3$. During the creation of the plasma, electron-ion pairs are produced through primary electron-impact ionization of the bulk molecules, such as $e + N_2 \Rightarrow e + N_2^+$ and $e + O_2 \Rightarrow e + O_2^+$, and the corresponding dissociative ionization processes for N_2 and O_2. The charge exchange reaction of positive ions, such as N_2^+, with the background O_2 is fast, resulting in mostly O_2^+ ions: $N_2^+ + O_2 \Rightarrow N_2 + O_2^+$. The positive ions react with Cl^- through the neutralization reactions: $Cl^- + O_2^+ \Rightarrow Cl + O_2$ and $Cl^- + O_2^+ \Rightarrow Cl + 2O$. In the absence of scavenging reactions for CCl_3, the input energy would be wasted because Cl and CCl_3 would simply recombine quickly to reform the original pollutant: $Cl + CCl_3 \Rightarrow CCl_4$. Fortunately, the presence of O_2 scavenges the CCl_3 through the fast reaction: $CCl_3 + O_2 \Rightarrow CCl_3O_2$. The CCl_3O_2 species reacts with Cl and, through a series of reactions, eventually produces $COCl_2$ (phosgene) as one of the main organic products. The other major product is Cl_2 which is formed by the reaction $Cl + Cl + M \Rightarrow Cl_2 + M$.

An analysis of the rates of the reactions discussed above suggests that the energy consumption for CCl_4 removal is determined by the energy consumption (or G-value) for creating electron-ion pairs. The G-value (yield/100 eV) for ionization of dry air in an electron beam reactor is fairly well known. For a discharge reactor, such as a pulsed corona reactor, the effective G-value for ionization is determined by an effective electron mean energy (or an effective reduced field, E/N) in the discharge plasma. Since the electric field distribution in the microdischarges (streamers) is strongly non-uniform and time-dependent, it may seem necessary to determine the spatial and temporal structure of the microdischarge plasma, as well as its dependence on external parameters such as electrode geometry and voltage pulse parameters, before one can make any useful scaling predictions. Our theoretical and experimental work using dilute mixtures of NO in N_2 and in N_2/O_2 mixtures suggest that because the streamer plasma is space-charge shielded, the electron mean energy in the plasma channels weakly depends on the electrode structure, applied peak voltage, and whether the microdischarges are extinguished because of the short voltage pulse (as in pulsed corona) or because of dielectric charging (as in silent discharge). Furthermore, we have determined that the effective electron mean energy in discharge reactors is around 4 eV. Using this effective electron mean energy we calculated the G-values for ionization processes in a pulsed corona reactor and compared them to those in an electron beam reactor.

REACTION	Electron Beam	Pulsed Corona
$e + N_2 \Rightarrow 2e + N(^4S) + N^+$	0.345	$< 10^{-6}$
$e + N_2 \Rightarrow 2e + N(^2D) + N^+$	0.345	$< 10^{-6}$
$e + N_2 \Rightarrow 2e + N_2^+$	2.27	0.044
$e + O_2 \Rightarrow 2e + O_2^+$	2.07	0.170
$e + O_2 \Rightarrow 2e + O(^1D) + O^+$	1.23	0.0016

For electron beam processing of dry air, these G-values correspond to an energy consumption of 33 eV per electron-ion pair produced. For pulsed corona processing, the energy consumption is around 1440 eV per electron-ion pair. As shown in the following figure, these values agree very well with our experimentally observed energy consumption values for CCl_4 removal in dry air.



These results demonstrate that for VOCs requiring copious amounts of electrons for decomposition, non-thermal plasma processing using an electron beam reactor is much more energy efficient than that using an electrical discharge reactor.

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